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EFFECTS OF THERMAL ANNEALING AND LONG-TERM AGEING ON ELECTRONIC DEFECTS IN CdSe THIN FILMS

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Defect distributions in CdSe thin films, 'as deposited', following thermal annealing, and after 10 years' storage under room conditions are investigated. Steady-state photoconductivity measurements at low temperatures suggest a decrease in the density of 'slow' recombination centres following annealing or storage. Transient photocurrent and thermally stimulated current spectroscopies reveal a peak in the density of states at 0.65 eV below the conduction band edge in the as-deposited film. This broadens and shifts towards the conduction band edge on annealing. Stored films exhibit an almost flat defect distribution, which may result from a combination of both types of defect. Raman scattering measurements suggest that both storage and annealing result in increased structural order.

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1. Introduction

The use of semiconducting thin films in gas sensor applications is well-established [1]. Frequently, the property measured is the dark conductivity, which is governed by a combination of charge carrier density and carrier mobility. Adsorbed gases may cause a change in the carrier concentration directly, by introducing donors or acceptors, or indirectly, by altering the concentration of electronic defects or by surface band-bending through the electrostatic effect of polar molecules. The presence of adsorbates also influences the photoconductive [2] and photoluminescent [3] properties of films such as CdS and CdSe.

In order to develop films that are suitable for sensor applications, in terms of sensitivity, reproducibility and stability, it is important to identify and understand how the film properties are influenced by long-term exposure to ambient conditions, and by other treatments such as thermal annealing. We report here on the effects of thermal annealing and long-term (10 year) storage under room conditions ('ageing') of thermally-evaporated microcrystalline CdSe films. By measuring the dark current, steady-state photocurrent, transient photocurrent and thermally-stimulated currents, we deduce a semi-quantitative picture of how the distribution of electronic defects is influenced by these treatments, and suggest possible origins in terms of existing models.

2. Experimental details

CdSe films of nominal thickness 200 nm were deposited at a rate of 0.5 nm/s by thermal evaporation onto Corning 7059 glass substrates maintained at room temperature. X-ray diffraction

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measurements indicated that as-deposited films consist perdominantly of cubic microcrystals dispersed in a highly disordered matrix. The optical band gap at 293 K was measured as 1.6 eV, about 0.15 eV lower than that of CdSe monocrystals. This suggests a high concentration of band tail states. Details of the deposition system and procedures, and the structural characterisation of the CdSe films are described more fully elsewhere [4]. Measurements were carried out on 'as-deposited' and 'aged' (10 years under ambient conditions) films, deposited under identical conditions, and also on 'as-deposited' films annealed for 60 minutes in Ar at either 200 or 400 ^{o}C.

Sputtered gold contacts about 1 cm long and spaced 0.15 cm apart were deposited on top of the layers used for electrical measurements. Linear current-voltage characteristics were obtained at applied voltages up to 500 V. Steady state photocurrent (SSPC) measurements were made using monochromatic light from a red LED (λ = 625 nm, $F = 10^{15}$ s^{-1} cm^{-2}), incident normal to the layer surface. In measurements of thermally stimulated currents, the sample temperature was increased at a rate of 0.05 K/s.

For transient photocurrent (TPC) measurements, an electrically screened Laser Science VSL-337 N_2 laser plus dye attachment was used to generate 4 ns pulses of 500 nm light at a flux of 2×10^{14} cm^{-2}, attenuated as required by means of neutral density filters. Following preamplification, the photocurrent decay at 300 V dc bias was recorded on a Tektronix TDS3052 storage oscilloscope and the data were transferred to a PC for analysis. Measurements in the range 128 to 423 K were made in a screened vacuum cryostat. [5].

3. Results and discussion

The temperature dependence of the mobility-lifetime product ($\mu\tau$) calculated from the SSPC is shown in Fig. 1. At temperatures below 180 K an overall photoconductivity decrease was observed with increasing annealing temperature. This implies that the concentration of 'slow' recombination centres, which are known to limit the low-temperature photoconductivity, decreases with increasing annealing temperature. These centres are located about 0.6 eV above the valence band [4,6] and are usually associated with Cd vacancies. Hence it is concluded that annealing causes some rearrangement in the network of CdSe microcrystals. Moreover, annealing at 200^{o}C did not change the dark conductivity of the films in comparison with 'as-deposited' ones, but annealing at 400^{o}C caused a conductivity increase of 2 to 3 orders of magnitude. It is known that at 400^{o}C, recrystallization of CdSe occurs. In this, there is a lattice transformation from a cubic to a hexagonal structure, an increase in the microcrystal size, and an overall improvement of the lattice order. Also, some Se re-evaporation from the film surface (and creation of Se vacancies i.e. donors [7]) may occur, which could account for the observed conductivity increase.

TPC decays obtained from 'as-deposited' and annealed CdSe films are shown in Fig. 2a. These exhibit a rapid initial decrease in photocurrent, of 2 to 3 orders of magnitude within the first 100 ns, followed by a more gradual fall. Analysis of the photocurrent decays has been made in terms of multiple-trapping, using the Fourier-transform density of states (DOS) spectroscopy [5]. The defect distribution obtained for the samples studied here is shown in Fig. 2b. The energy scaling of the DOS plot was carried out assuming an attempt-to-escape frequency of 1×10^{12} s^{-1}, since this gave reasonable agreement at different temperatures. The absolute scaling of the DOS is difficult to deduce however, as a number of factors such as the capture cross-section of the defects and the carrier mobility must be known. Thus the DOS *magnitudes* are at best only relative. However, one can see a significant difference in the *shape* of the DOS distribution in the 'as-deposited' and annealed samples. A maximum at about 0.65 eV below the conduction band edge is evident in the 'as-deposited' film data. Following annealing, this feature disappears and a broader distribution peaked at 0.4-0.5 eV emerges.

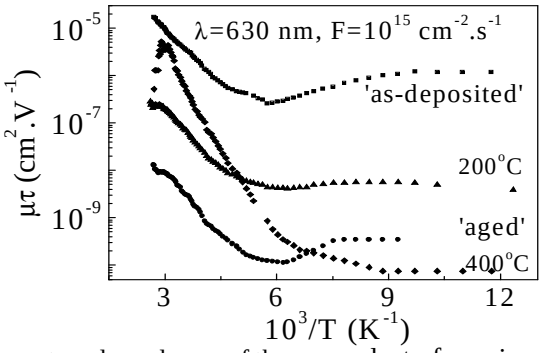

Fig. 1. Temperature dependences of the μτ product of a series of CdSe thin films.

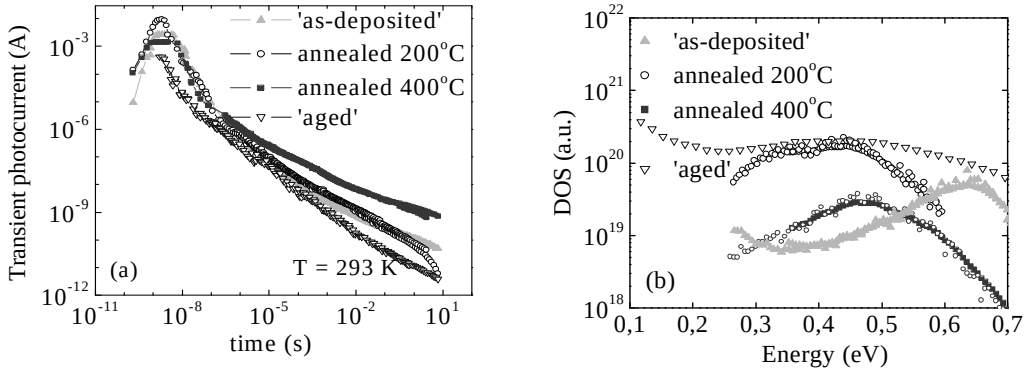

Fig. 2. (a) Transient photocurrent decays at room temperature from 'as-deposited', annealed (200 and 400 °C) and 'aged' CdSe thin films; (b) Defect distributions from Fourier-transform transient photocurrent spectroscopy applied to the TPC decays in (a).

Comparison of the resulting DOS distributions suggests that the 'aged' sample exhibits features associated with both the 'as-deposited' and annealed films. The DOS distribution is quite broad, changing by no more than a factor of two between 0.25 and 0.7 eV. Data taken at 140 K show a TPC power-law decay index close to –1. This suggests [8] that the DOS is quite flat at energies as shallow as 0.1 eV below the conduction band edge. Thus there is no direct evidence for the band tailing, as is seen in (e.g.) amorphous silicon [5]. However, it should be borne in mind that the numerical Fourier integration central to the extraction of the DOS may be significantly in error if the decay at short times is steep, as is the case here, because a substantial contribution to the integral may not lie within the experimental time-scale [9]. This aspect needs to be examined in more detail.

Raman scattering results are shown in Fig. 3. Both the 1LO and the 2LO phonon band of the 'as-deposited' sample are asymmetric. The bands may be fitted with a Lorentzian (peaked at 210 cm^{-1}) and a Gaussian (peaked at ~ 420 cm^{-1}) for the two bands respectively, coinciding with the corresponding bands of CdSe monocrystals [7], plus a red-shifted Gaussian (due to scattering from nanocrystals [10]) for both lines. The greater symmetry of the bands in the 'aged' sample is therefore an indication of increased order, presumably through the formation of larger crystallites.

Fig. 4 shows thermally stimulated currents (TSC) measured on 'as-deposited' and 'aged' CdSe films. The TSC spectrum of the 'aged' sample displays a number of maxima, which largely coincide with those observed in polycrystalline CdSe [11]. In contrast, only one asymmetric broad band is seen in the spectrum of the 'as-deposited' CdSe film. The maximum of this is shifted to higher temperatures with respect to that of the high-temperature band of the 'aged' sample. One can estimate the depth of the traps in the forbidden gap using the following relation between the trap depth E_t and the temperature of the TSC maximum T_m: $E_t \sim 25kT_m$ [12]. A value of 0.65 eV corresponds to T_m = 300 K, which is in good agreement with the TPC DOS maximum of the 'as-deposited' sample (Fig. 2b). Moreover, the TSC shape resembles the DOS shape. As for the 'aged' sample, keeping in mind that the μτ product decreases with temperature up to ~200 K and then gradually increases (see Fig. 1), one can assume a nearly flat DOS, which is in good agreement with the TPC result.

4. Conclusions

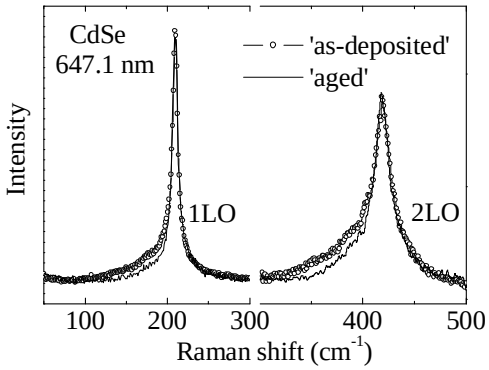

Fig. 3. Raman scattering spectra of 'as-deposited' and 'aged' CdSe films. The 647.1 nm line of a Kr^+ laser was used for excitation.

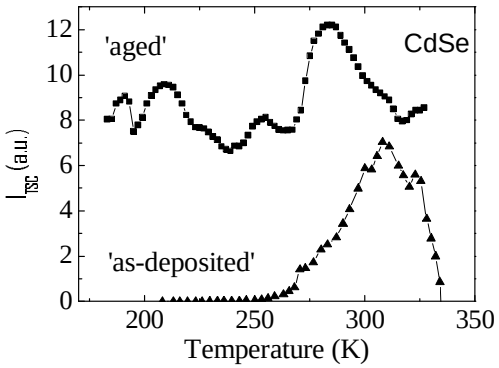

Fig. 4. Thermally stimulated currents of 'as-deposited' and 'aged' CdSe single layers.

TPC and TSC measurements carried out on CdSe thin films indicate that thermal annealing or storage at room temperature cause a similar reduction of the defect states at ~0.65 eV below the conduction band edge. The SSPC results at low temperatures indicate that annealing decreases the concentration of slow recombination centres, usually related to Cd vacancies and situated at ~0.6 eV above the valence band edge. Raman scattering measurements reveal a greater crystalline order in stored films. This structural information is consistent with the reduction in the density of defect states inferred from TPC and TSC. The dark conductivity increase observed upon annealing at 400 ºC implies some Se re-evaporation from the film surface.

Acknowledgements

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